

Approaching Bulk Limit for Three-Dimensional Solids via the Cyclic Cluster Approximation: Semiempirical INDO Study

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ABSTRACT: The cyclic cluster method has been examined for a number of solids using a recently developed computer code, SOLID98. Calculations are based on the quasirelativistic (QR) INDO/1 (intermediate neglect of differential overlap) method that is simple enough to allow for a saturation of the (cyclic) clusters. Convergence toward the bulk limit (INDO/1) charge density with respect to the size of the model cyclic cluster is shown for diamond, silicon, germanium, boron nitride, gallium phosphide, gallium arsenide, and gallium antimonide. Results show that, as soon as the initial cluster size reaches 5 to 6 nm, one can safely use the obtained density matrix as a good approximation to the bulk limit. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 253–261, 1999

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Nowadays, extended systems, until this point the domain of solid-state physicists, have also become more and more subject to the rapidly growing interest of computational chemists. Systems with translational periodicity are of special interest for the physics and chemistry of materials, as well as for crystallography or mineralogy. Computer codes developed during the last 15 to 20 years to treat such systems with *ab initio* and/or density-functional-based methods^{1,2} together with new computer technologies allowed for an amazing breakthrough of commonly established *molecular methods* to the world of periodic three-dimensional systems. These methods are based on either the transformation of a localized basis to periodic Bloch orbitals, or the use of the plane-wave basis², or a combination of both. Such an approach finally results in the factorization of the problem in reciprocal space. Nevertheless, the quality of the results depends strongly on how well the interactions of the reference unit cell are described.

To obtain results that correspond closely to the infinite bulk limit (at least within a given computational method), one has to include a rather large number of neighboring unit cells. On the other hand, one often needs to handle very large unit cells for complicated substances or defective structures. Computational demands then quickly reach prohibitive limits. Due to the simplicity and a potential to treat large unit cells, a semiempirical approach remains up to date for periodic structures, as well as for very large molecular systems. This assessment is supported by recent detailed studies of doped fullerenes^{3,4} using the previously reported semiempirical INDO-based program.⁵ In this study we report on our recently developed computer code⁶ to treat three-dimensional periodic systems within the quasirelativistic (QR) INDO/1 scheme, whose very simple parameterization is based on the results of atomic Dirac-Fock calculations^{7,8}. As a starting point, we have revived the rather old idea of the cyclic cluster approach (CCA) (see, e.g., a review by Deák⁹). A relatively recent study by Chandrasekhar and Das¹⁰ on one-dimensional polymers has shown a rather rapid convergence of the energy and other properties toward the bulk limit with respect to the size of the (cycled) linear chains. To our knowledge, up to convergence, such a study has not yet been done for three-dimensional systems, which is the purpose of the present report.

The model given is easy to understand, and it is also suitable for use by novices without much knowledge about space groups or translational symmetry.

After a recapitulation of the theoretical background, we briefly discuss the algorithm and, finally, using examples, we examine the reliability of the cyclic cluster model for three-dimensional systems and show the convergence of the results with respect to calculated cluster size.

Theoretical Background

MODEL

The basic idea of the present model is very simple. It starts from a well-established approach used by many computational chemists to represent the bulk by a possibly large cluster, which is a cut-out of the solid. Such a cluster is finite and, even if it is constructed from formally equal units, the effect of the boundary is too strong near the center of the cluster. Consequently, the convergence of a calculated property with the size of the cluster toward the bulk limit may be extremely slow. This is often complicated by the need to saturate the boundary bonds (e.g., by hydrogen atoms or other terminal groups), which again changes the picture of the electronic structure.

Let us assume a cluster constructed from a chosen atomic structure—the unit cell—by replicating the latter N_1 , N_2 , and N_3 times in three respective lattice vector directions \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . Thus, the cluster is built from $N = N_1 \cdot N_2 \cdot N_3$ unit cells, which basically differ in their surroundings. Of course, in a periodic system, which we are attempting to model, all the unit cells have equal surroundings. The idea behind the cyclic cluster approach is to impose such equal surroundings on all of the units in the cluster constructed. In one dimension this resembles a ring, which, in the infinite limit, changes to a translationally periodic chain. This rather simple approach was first applied many years ago in chemisorption theory of graphite and boron nitride in conjunction with extended Hückel theory¹¹ and CNDO/2 (complete neglect of differential overlap).¹² Shortly thereafter, the model was analyzed extensively for one- and two-dimensional systems by Zunger.¹³

Having a translationally periodic structure permits transformation of the atomic orbital basis

($|p^{\mathbf{R}}\rangle$) to periodic Bloch orbitals:

$$|p^{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |p^{\mathbf{R}}\rangle \quad (1)$$

whose linear combinations are known as the crystal orbitals (CO)^{14,15}; that is, periodic counterparts of the molecular orbitals. From eq. (1):

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (2)$$

and $|p^{\mathbf{R}}\rangle$ means an atomic orbital in a unit cell defined by the translation \mathbf{R} . \mathbf{k} is the reciprocal vector, given as:

$$\mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 \quad (3)$$

where the reciprocal lattice vectors \mathbf{b}_j fulfill $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, with δ_{ij} being the Kronecker delta. n_i , m_i in eqs. (2) and (3) are integer numbers. It is natural (although mathematically not inevitable) to take the central unit of the cluster as the reference, hence, for odd N_i , we can use a convention:

$$m_i, n_i = -(N_i - 1)/2, \dots, 0, \dots, (N_i - 1)/2 \quad (i = 1, 2, 3).$$

Obviously, with increasing N_i one approaches the bulk. Hence, for $N_i \rightarrow \infty$ (bulk limit) the translational symmetry is guaranteed. Instead, for a finite cluster, a ring periodicity is imposed by:

$$\mathbf{R} + \mathbf{R}' = \sum_{i=1}^3 \left\{ n_i + n'_i - N_i \cdot \text{int} \left(\frac{2(n_i + n'_i)}{N_i} \right) \right\} \mathbf{a}_i \quad (4)$$

$\text{int}(\cdot)$ is the integer part. Based on eq. (4), any translation given as a sum of two translations within a cluster is again returned to the given cluster. Relation eq. (4) corresponds to what is known as the periodic boundary condition (PBC). So that each unit cell experiences the surroundings of the reference cell, we require:

$$\langle p^{\mathbf{R}+\mathbf{R}'} | \hat{h} | q^{\mathbf{R}'} \rangle = \langle p^{\mathbf{R}} | \hat{h} | q^{\mathbf{0}} \rangle = h_{pq}^{\mathbf{R}\mathbf{0}} \quad (5)$$

$$\langle p^{\mathbf{R}_1+\mathbf{R}'} q^{\mathbf{R}_2+\mathbf{R}'} | \hat{g} | r^{\mathbf{R}'} s^{\mathbf{R}_3+\mathbf{R}'} \rangle = \langle p^{\mathbf{R}_1} q^{\mathbf{R}_2} | \hat{g} | r^{\mathbf{0}} s^{\mathbf{R}_3} \rangle \quad (6)$$

with \hat{h} , \hat{g} the one- and two-electron parts of the Hamiltonian, respectively. Any \mathbf{R} is defined by eq. (2) and $\mathbf{0}$ ($n_1 = n_2 = n_3 = 0$) refers to the reference unit cell.

Evidently, eqs. (5) and (6) are not valid for a finite cluster. Imposing surroundings of the reference unit to all units in the cluster means replacing the integrals from the left-hand side of eqs. (5) and (6) with the values from the right-hand side. For unambiguous assignments we require:

$$S_{pq}^{\mathbf{0}\mathbf{R}} = S_{pq}^{-\mathbf{R}\mathbf{0}} \quad (7)$$

$$h_{pq}^{\mathbf{0}\mathbf{R}} = h_{pq}^{-\mathbf{R}\mathbf{0}} \quad (8)$$

$$\begin{aligned} \langle p^{\mathbf{R}_1} q^{\mathbf{R}_2} | \hat{g} | r^{\mathbf{0}} s^{\mathbf{R}_3} \rangle &= \langle p^{\mathbf{0}} q^{\mathbf{R}_2-\mathbf{R}_1} | \hat{g} | r^{-\mathbf{R}_1} s^{\mathbf{R}_3-\mathbf{R}_1} \rangle \\ &= \langle p^{\mathbf{R}_1-\mathbf{R}_2} q^{\mathbf{0}} | \hat{g} | r^{-\mathbf{R}_2} s^{\mathbf{R}_3-\mathbf{R}_2} \rangle \\ &= \langle p^{\mathbf{R}_1-\mathbf{R}_3} q^{\mathbf{R}_2-\mathbf{R}_3} | \hat{g} | r^{-\mathbf{R}_3} s^{\mathbf{0}} \rangle \end{aligned} \quad (9)$$

where S is the overlap. Whereas eq. (7) is always valid, for the exact Hamiltonian, eq. (8) is only fulfilled for clusters with a center of symmetry. Eqs. (9) are trivially valid for two-center, two-electron integrals. Using eq. (4) it is obvious that eqs. (9) are not generally fulfilled for three- and four-center two-electron integrals. In *ab initio* cyclic cluster calculations this problem must be solved; for example, via averaging of integrals¹⁶, whereas, with ZDO (zero differential overlap) approximation, such a problem disappears, because eq. (8) is always true, and only two-center two-electron integrals are involved. Perhaps due to the latter aspect, little attention has so far been directed toward the aforementioned problem in (semiempirical) cyclic cluster calculations.

Another point that is especially relevant for two- and three-dimensional systems is the violation of the point-symmetry properties for the matrix elements, which should be a prerequisite in any two- or three-dimensional calculation.^{17,18} Of course, this problem is essentially eliminated (at least numerically) as the cluster approaches infinity. In view of our results, a saturated cluster is still computationally tractable in this sense.

Having eqs. (5) and (6) fulfilled permits transformation of the usual Fock matrix to a Bloch basis, which leads to factorizing the problem into N blocks of the dimension $n_c \times n_c$ (where n_c is number of atomic orbitals per cell)¹⁴:

$$F_{pq}^{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'} F_{pq}^{\mathbf{k}} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} F_{pq}^{\mathbf{R}\mathbf{0}} \quad (10)$$

whose diagonalization provides the crystal orbitals for the given \mathbf{k} -point symmetry. For the sake of completeness, it is emphasized that for closed-shell

systems:

$$F_{pq}^{R0} = h_{pq}^{R0} + \sum_{\substack{\mathbf{R}_1, \mathbf{R}_2 \\ (\mathbf{R}_3 = \mathbf{R}_1 - \mathbf{R}_2)}}^N \sum_{r,s}^{\text{cell}} P_{rs}^{R30} (2 \langle p^{\mathbf{R}} r^{\mathbf{R}_1} | \hat{g} | q^0 s^{\mathbf{R}_2} \rangle - \langle p^{\mathbf{R}} r^{\mathbf{R}_1} | \hat{g} | s^{\mathbf{R}_2} q^0 \rangle) \quad (11)$$

$$P_{pq}^{R0} = \frac{1}{N} \sum_{\mathbf{k}}^N e^{i\mathbf{k} \cdot \mathbf{R}} P_{pq}^{\mathbf{k}} \quad (12)$$

$$P_{pq}^{\mathbf{k}} = \sum_m^{\text{occ}} (c_{pm}^{\mathbf{k}})^* c_{qm}^{\mathbf{k}} \quad (13)$$

where $c_{pm}^{\mathbf{k}}$ are the occupied CO coefficients for the given \mathbf{k} -point symmetry.

The difference between the established CO techniques^{5,19} and the cyclic cluster approach is essentially in the evaluation of the density matrix in the direct space, eq. (12). For the bulk limit, the summation is changed to integration over the Brillouin zone. In established band structure calculations the integration is practically evaluated via a discrete summation from preselected \mathbf{k} -points (special points).^{20–23} In contrast, the present model always contains a discrete sum with N \mathbf{k} -points uniquely defined by the cluster via translations in the reciprocal space defined by eq. (3). Therefore, instead of special points, the latter corresponds to a homogeneous distribution of \mathbf{k} -points. In the present CCA model, the integrals (and all interactions) are evaluated only within the finite cluster. Unlike for established band structure methods, no cut-off procedures²⁴ or tail-expansion techniques²⁵ or Madelung-type sums⁵ are needed.

Having the cluster “saturated” (i.e., if the results do not change with its further extension), we can safely assume that the density matrix corresponds to the bulk limit, as well as the Fock matrix constructed from it. Accordingly, transformation of the (direct space) Fock matrix to any \mathbf{k} -point symmetry is relevant (i.e., the full band structure calculation for required symmetry direction) as well. For the one-dimensional case, such an approach was applied by Chandrasekhar and Das.¹⁰

INDO/1 FORMULATION IN CYCLIC CLUSTER APPROXIMATION

The (QR) INDO/1,^{7,8} as is the case with most semiempirical methods, is a valence electron approach based on a ZDO approximation. For simplicity, we do not change the notation, but hereafter h denotes the core Hamiltonian (i.e., $h \rightarrow h^{\text{core}}$). Irrespective of a particular parameterization,

the Fock matrix for a closed-shell molecular system is (see, e.g., ref. 26):

$$F_{p_A p_A} = h_{p_A p_A} + \sum_{q,r} P_{q_A r_A} (2 \langle p_A q_A | \hat{g} | p_A r_A \rangle - \langle p_A p_A | \hat{g} | q_A r_A \rangle) + 2 \sum_q \sum_{C \neq A} P_{q_C q_C} \langle p_A q_C | \hat{g} | p_A q_C \rangle \quad (14)$$

$$F_{p_A q_A} = h_{p_A q_A} + \sum_{r,s} P_{r_A s_A} (2 \langle p_A r_A | \hat{g} | q_A s_A \rangle - \langle p_A r_A | \hat{g} | s_A q_A \rangle) \quad (15)$$

$$F_{p_A q_B} = h_{p_A q_B} - P_{p_A q_B} \langle p_A q_B | \hat{g} | p_A q_B \rangle \quad (16)$$

where subscripts A , B , and C denote different atoms. In the present variant of INDO, the one- and two-center Coulomb integrals, as well as the one-center exchange and hybrid two-electron integrals, are calculated using the STO (Slater-type orbitals) basis with exponents obtained from Dirac–Fock calculations on atoms.⁸ The diagonal part of the core Hamiltonian is given by:

$$h_{p_A p_A} = U_{p_A} - \sum_{C \neq A} \sum_{q_C} P_{q_C q_C}^{\text{free}} \langle p_A q_C | \hat{g} | p_A q_C \rangle \quad (17)$$

$P_{q_C q_C}^{\text{free}}$ is the occupation number (0, 1, 2) for the given orbital in the *free* atom. The second sum is a usual approximation of the two-center electron-nuclear attraction. U_{p_A} is an approximation for the kinetic part and the one-center repulsion integrals. In the present variant of INDO, the U_{p_A} is expressed through atomic orbital energies generated by the Dirac–Fock calculations and averaged one-center repulsion integrals in terms of Slater–Condon parameters. Eq. (15) corresponds to the Goeppert–Mayer–Sklar approximation²⁷; that is, so-called penetration effects are neglected. Details can be found elsewhere.^{8,28}

Many ZDO-type methods that have found a broader use closely follow the original proposal of Pople et al.²⁶ according to which off-diagonal matrix elements of the one-electron core operator are not strictly subject to the ZDO approximation, but are usually expressed through a set of atomic (or atomic orbital) β parameters. In the (QR) INDO/1 (or CNDO/1), an alternative approximation is applied:

$$h_{p_A q_B} = -\frac{1}{2} S_{p_A q_B} \left(\frac{\zeta_{p_A}}{n_{p_A}} + \frac{\zeta_{q_B}}{n_{q_B}} \right) \cdot K \quad (18)$$

where ζ is the exponent of the Slater-type atomic orbital and n (here, exceptionally) denotes the

principal quantum number. $S_{p_A q_B}$ is the overlap integral between atomic orbitals, p_A and q_B , and K is a scaling constant that is set to $K = 1.2$ as a compromise value to reasonably reproduce the geometry and the band structure parameters. Basically, in the original INDO there are semiempirically determined β parameters in eq. (18), instead of ζ/n . Whatever the established approximation, the averaging of some atomic parameters, such as in eq. (18), finally guarantees that eq. (8) is valid, because of the validity of eq. (7). Consequently, one can uniquely assign equal interactions to all units in the cluster, and preserve the modular periodicity. With our choice of the reference cell the interactions never exceed the *half dimensions* of the cluster, but they are not restricted to a specific range around the atoms given by the interaction radius.

Based on the foregoing, it is obvious to reformulate eqs. (14)–(16) for the cyclic cluster to have an (INDO) equivalent for eq. (11). Noting that, $P_{pq}^{\text{RR}} = P_{pq}^{\text{OO}}$ in the periodic cluster, one finally arrives at:

$$F_{p_A p_A}^{\text{OO}} = h_{p_A p_A}^{\text{OO}} + \sum_{q, r} P_{q_A r_A}^{\text{OO}} (2 \langle p_A^0 q_A^0 | \hat{g} | p_A^0 r_A^0 \rangle - \langle p_A^0 p_A^0 | \hat{g} | q_A^0 r_A^0 \rangle) + 2 \sum_q \sum_C^{\text{cell}} P_{q_C q_C}^{\text{OO}} J_{p_A q_C} \quad (19)$$

$$F_{p_A q_A}^{\text{OO}} = h_{p_A q_A}^{\text{OO}} + \sum_{r, s} P_{r_A s_A}^{\text{OO}} (2 \langle p_A^0 r_A^0 | \hat{g} | q_A^0 s_A^0 \rangle - \langle p_A^0 r_A^0 | \hat{g} | s_A^0 q_A^0 \rangle) \quad (20)$$

$$F_{p_A q_B}^{\text{RO}} = h_{p_A q_B}^{\text{RO}} - P_{p_A q_B}^{\text{RO}} \langle p_A^{\text{R}} q_B^{\text{O}} | \hat{g} | p_A^{\text{R}} q_B^{\text{O}} \rangle \quad \text{for } B^{\text{R}} \neq A^{\text{O}} \quad (21)$$

with

$$J_{p_A q_C} = \sum_{\mathbf{R}} \langle p_A^{\text{O}} q_C^{\text{R}} | \hat{g} | p_A^{\text{O}} q_C^{\text{R}} \rangle \quad (A \neq C) \quad (22)$$

$$J_{p_A q_A} = \sum_{\mathbf{R} \neq 0} \langle p_A^{\text{O}} q_A^{\text{R}} | \hat{g} | p_A^{\text{O}} q_A^{\text{R}} \rangle \quad (23)$$

The electronic energy per cell is then expressed straightforwardly as:

$$E_{\text{el}}^{\text{cell}} = \sum_{p, q} P_{pq}^{\text{OO}} (h_{pq}^{\text{OO}} + F_{pq}^{\text{OO}}) + \sum_{\mathbf{R} \neq 0} \sum_{p, q} P_{pq}^{\text{RO}} (h_{pq}^{\text{RO}} + F_{pq}^{\text{RO}}) \quad (24)$$

and for the core–core repulsion per unit cell we have:

$$E_{\text{core}}^{\text{cell}} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A^{\text{core}} Z_B^{\text{core}}}{|\mathbf{r}_{AB}|} + \sum_{\mathbf{R} \neq 0} \sum_{A, B} \frac{Z_A^{\text{core}} Z_B^{\text{core}}}{|\mathbf{R} + \mathbf{r}_{AB}|} \quad (25)$$

where Z_A^{core} is the core charge for atom A and \mathbf{r}_{AB} is the interatomic distance vector within the unit cell. The total energy per cell ($E_{\text{tot}}^{\text{cell}}$) is obviously given as the sum of the former two. The first sums in eqs. (24) and (25) correspond to intracell energies, whereas the second sums correspond to the interaction with the rest of the cluster.

IMPLEMENTATION

From the computational point of view, it is clear that creation of the Fock matrix (in the case of INDO) is, from the computational point of view, merely negligible, because the one-center matrix elements, eqs. (19) and (20), are evaluated only within the reference cell, and the parallel vector multiple (P with Coulomb integrals) in eq. (21) is undoubtedly extremely fast. Transformation of F to \mathbf{k} -space eq. (10) and of $P^{\mathbf{k}}$ to direct space eq. (12) is simplified using the Euler relation (Re and Im are real and imaginary part, respectively):

$$Re(F_{p \geq q}^{\mathbf{k}}) = F_{p \geq q}^{\text{OO}} + \sum_{\mathbf{R} \neq 0}^{(N-1)/2} \cos(\mathbf{kR}) (F_{p \geq q}^{\text{RO}} + F_{p \geq q}^{-\text{RO}}) \quad (26)$$

$$Im(F_{p > q}^{\mathbf{k}}) = \sum_{\mathbf{R} \neq 0}^{(N-1)/2} \sin(\mathbf{kR}) (F_{p > q}^{\text{RO}} - F_{p > q}^{-\text{RO}}) \quad (27)$$

$$P_{p \geq q}^{\text{RO}} + P_{p \geq q}^{-\text{RO}} = \frac{2}{N} \sum_{\mathbf{k}}^{(N+1)/2} n \cdot \cos(\mathbf{kR}) Re(P_{p \geq q}^{\mathbf{k}}) \quad (28)$$

$$P_{p > q}^{\text{RO}} - P_{p > q}^{-\text{RO}} = \frac{2}{N} \sum_{\mathbf{k}}^{(N+1)/2} n \cdot \sin(\mathbf{kR}) Im(P_{p > q}^{\mathbf{k}}) \quad (29)$$

where $n = 1$ for $\mathbf{k} \equiv (0, 0, 0)$, and $n = 2$ for all other cases. Summations run either over one-half of the cluster \mathbf{R} or over one-half of the *reciprocal cluster* (Brillouin zone). From the last two equations, one easily obtains P_{pq}^{RO} . An optimal algorithm can be achieved if the matrix elements for RO and $-\text{RO}$ are arranged in either two different arrays, or back-to-back in a single array, as it is done in our case.

The code is neither necessarily limited to INDO nor to the cyclic cluster approach. Nevertheless, our primary goal has been testing of the cyclic cluster concept more than, to our knowledge, has been done before; that is, to eventually approach the “saturated” cluster limits. Due to its computational ease, the INDO approach permits such calculations.

Results and Discussion

Because the reliability of the INDO approach in solid-state calculations has been tested previously,⁵ we will focus our attention mainly on the applicability of the cyclic cluster approach in three dimensions. Our test systems include diamond, silicon, germanium, boron nitride, gallium arsenide, gallium antimonide, and gallium phosphide, whose structures correspond to a face-centered cubic Bravais lattice. Some of these have been studied extensively, and thus some comparative data are available.

We used a primitive unit cell (including two atoms) as a reference. Naturally, we used clusters of $N_1 \times N_2 \times N_3$ with $N_1 = N_2 = N_3$. To investigate the convergence pattern with the size, we started from the smallest appropriate periodic cluster of $N_i = 3$ and proceeded with increasing N_i until the energy change was less than 0.001 eV. For diamond, we went as far as $N_i = 35$ to test the stability and progression of the CPU time consumption. For each cluster, the energy was converged to 10^{-9} eV. We used experimental lattice parameters in this convergence study, although, for the saturated cluster, we also performed optimization of

TABLE I. QR-INDO-Optimized Lattice Parameters ($a \times 10^{10}$ / m) Compared with Experimental Ones.

Compound	Optimized	Experimental ²⁹	Δ (%) ^a
Diamond	3.686	3.567	3.3
Si	5.402	5.431	−0.5
Ge	5.463	5.658	−3.4
BN	3.809	3.615	5.3
GaP	5.369	5.451	−1.5
GaAs	5.461	5.653	−3.4
GaSb	5.780	6.096	−5.2

^aRelative deviation from experiment.

lattice parameters. Experimental and QR-INDO-optimized lattice parameters are given in Table I. The error of the optimized structures corresponds to what may be expected from the semiempirical method.

The convergence of the energy per cell, as well as for the energy band gap for all systems studied, is shown in Tables II and III. Energy convergence is surprisingly rapid and, with this energy convergence, a size of 7 to 9 units in each direction is reliable for all systems investigated to be accurate to 0.01 eV. This means having three to four neighboring units in each direction, which corresponds to an approximate interaction radius of 0.8 to 1.6 nm, going from diamond to gallium antimonide. Slower convergence is seen for the highest occupied–lowest virtual energy band gap. Here, much more than for energy, the slower convergence with the size of the cluster is pronounced for the two semiconductors (silicon and germanium). To have a “saturated” cluster now means taking up to nine

TABLE II. Deviation of Cyclic Cluster Energy per Cell from Bulk limit (in eV)

N_i^a	C(d)	Si	Ge	BN	GaP	GaAs	GaSb
3	2.022	1.290	1.374	1.533	0.947	1.015	0.923
5	0.040	0.111	0.153	0.026	0.053	0.077	0.079
7	0.002	0.021	0.033	0.001	0.006	0.011	0.012
9	0.000	0.005	0.010	0.000	0.001	0.002	0.002
11	0.000	0.002	0.003	0.000	0.000	0.000	0.001
13	0.000	0.001	0.001	0.000	0.000	0.000	0.000
15	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Bulk ^b	−370.139	−236.965	−246.908	−399.988	−275.813	−264.561	−241.851

^aUsing the experimental lattice parameter; N_i is number of unit cells along a single translational vector, the size of the cluster is N_i^3 .
^bTotal QR-INDO energies per unit. Although these numbers have no meaning for the reader, we give them to indicate the relative error for various cyclic clusters.

neighbors in each direction around the reference cell, which corresponds to the cluster diameter of about 7 nm. Of course, the band gaps are taken from the *a posteriori* band structure calculation (including special points, as described earlier), which is the only relevant approach, because the ensemble of *k*-points generated in the CCA may not include the special point for which the gap is smallest. For comparison, in Table III, the results for the QR-INDO-optimized lattice, as well as some comparative data, are given. Experimental data correspond to excitation energies. For an independent particle model one can hardly expect generally good agreement of these values with experiment, because the electron correlation is important. As mentioned earlier, the single parameter in this QR-INDO approach has been set to reproduce reasonably both geometries and band gaps. Nevertheless, in Table III, at least one point is demonstrated, namely that the data calculated by the present approach fully fit to the dissipation of results from other methods, including *ab initio* treatment without electron correlation.

What is frequently of interest is the topology of the band structure. In Figure 1a–c we compare band structures along some special symmetry directions obtained from the CCA calculations using $N_i = 3, 5, 17$ for germanium, which is the slowest convergent species in our series. Initially, we did not want to include results for $N_i = 3$ (one neighbor), but as is evident, one can hardly recognize

any difference in the topology of bands going from $N_i = 5$ to $N_i = 17$, except for lowering the band gap and pushing the Fermi level (i.e., the midpoint between the highest filled and lowest empty one-electron state) slightly toward more negative values. The bottom bands did not differ at all. Hence, we have excluded them from the figure and instead show the bands around the Fermi level in a larger scale.

For $N_i = 3$, as compared with the other two, some lines are evidently split. This means that the degeneracy of those bands, otherwise guaranteed from point symmetry, does not occur (i.e., for $N_i = 3$ the point symmetry is obviously violated). It is encouraging that, even for a relatively small periodic cluster of size $5 \times 5 \times 5$, the point symmetry violation can be safely ignored, because the error is numerically very small.

Finally, in Table IV, we have collected typical CPU timings per iteration in the SCF procedure. As mentioned previously, with diamond we went as far as the cyclic cluster size of $35 \times 35 \times 35$, which includes more than 300,000 STO basis functions. The goal was to assess the numerical stability. Additional tests proved that, within our algorithm, the results are stable up to the cluster size of about 30 nm in one dimension. We must mention, however, that some intermediate values must be stored in quadruple precision. Relatively higher CPU-time progression for very large clusters is correlated with much more intensive IO operations, due to the lack of core memory.

TABLE III.
Occupied-Virtual Energy Band Gap as a Function of Cluster size (in eV).

N_i^a	C(d)	Si	Ge	BN	GaP	GaAs	GaSb
3	0.443	4.233	2.453	7.193	6.009	4.455	4.001
5	10.380	4.085	1.590	12.284	5.461	3.784	3.373
7	10.255	3.808	1.101	12.202	5.260	3.484	3.086
9	10.237	3.691	0.822	12.192	5.195	3.358	2.958
11	10.234	3.639	0.646	12.192	5.174	3.301	2.898
13	10.233	3.614	0.527	12.193	5.167	3.273	2.867
15	10.233	3.603	0.442	12.193	5.164	3.259	2.851
17	10.233	3.597	0.379	12.193	5.164	3.251	2.842
19	10.233	3.595	0.330	12.193	5.164	3.247	2.838
∞^b	10.233	3.592	0.250	12.193	5.163	3.243	2.835
CCA-INDO ^c	10.545	3.609	0.393	11.939	5.273	3.486	3.197
CO ^d	13.9	9.4		11.3			
CO-INDO ^e	9.2	5.8	1.9	13.4			
Exp. ^f	6.5	1.2	0.7	11.9	2.9	1.5	0.8

^aSee Table II. ^bEstimated limit. ^cCCA-QR-INDO / 1-optimized structure, $N_i = 19$. ^d*Ab initio* CO approach, values taken from refs. 30–32, respectively. ^eValues taken from ref. 5. ^fValues taken from ref. 29.

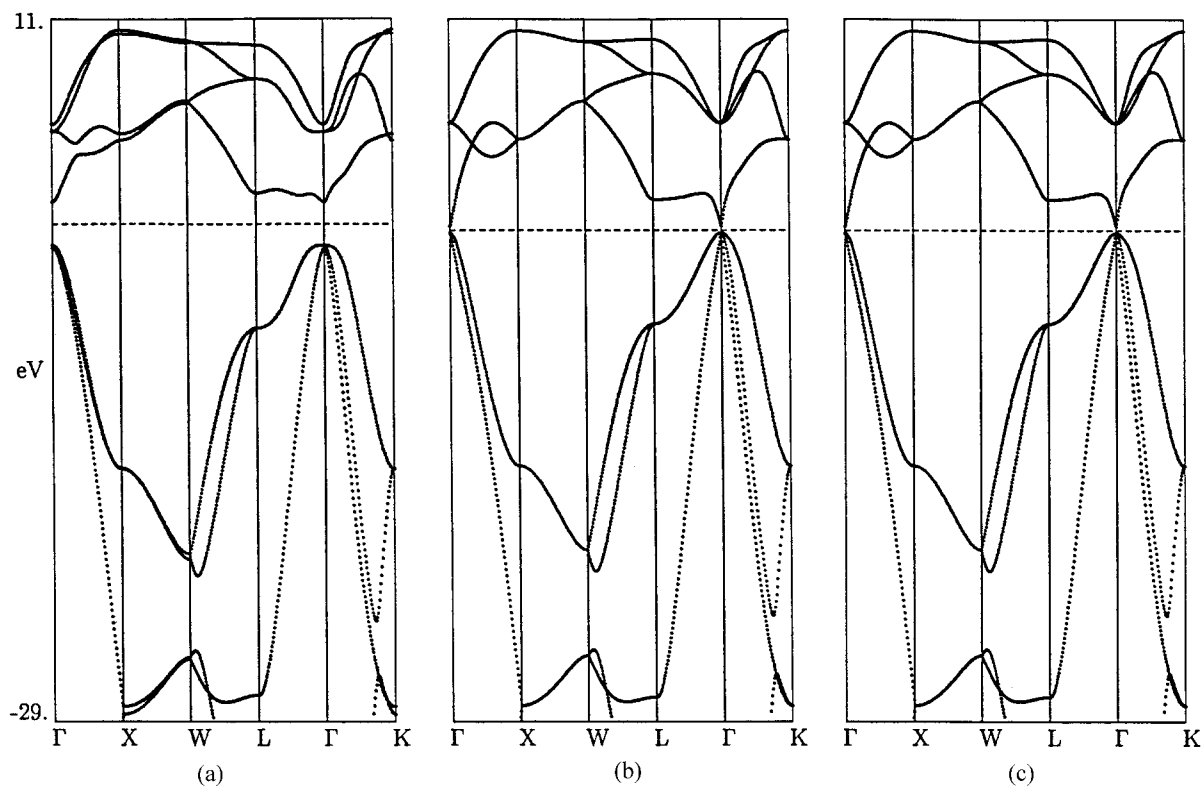


FIGURE 1. Band structure of germanium calculated by using the cyclic cluster size of $3 \times 3 \times 3$ (a), $5 \times 5 \times 5$ (b), and $17 \times 17 \times 17$ (c) unit cells. Fermi energy is denoted by the dashed line. Its values are -0.80 (a), -0.95 (b), and -1.18 eV (c).

TABLE IV.
Typical CPU Times — all Systems
(HP C160 / PA-8000).

N_i^a	Atoms	Orbitals	k -Points	CPU time / s ^b
3	54	216	14	0.02
5	250	1000	63	0.09
7	686	2744	172	0.44
9	1458	5832	365	1.67
11	2662	10648	666	5.58
13	4394	17576	1099	15.4
15	6750	27000	1688	42.9
17	9826	39304	2457	83.5
⋮				
29	48778	195112	12195	1400
⋮				
35	85750	343000	21438	6720

^aSee Table II. ^bCPU time per iteration. Typically, after 50 iterations, an accuracy of 10^{-8} eV was achieved for energy.

Conclusion

By means of our newly implemented program to treat solid-state periodic systems, we have investigated the cyclic cluster approach. In view of our results, the model can be used to simulate solids in a practical manner, because, at least in combination with semiempirical methods, the “saturated” cyclic cluster (i.e., one that formally corresponds to the bulk) is easily achievable. If the cluster is saturated, the problem with formal point symmetry violation for a cyclic cluster becomes irrelevant. Of course, the semiempirical methods have their own weaknesses. On the other hand, one is often faced with the problem of proper balance between the physical model used and the rigorousness of the applied computational method. Although our code is not necessarily connected to the QR-INDO, nor to the cyclic cluster approach, we believe this to be a well-balanced and straightforward combination for use with large systems. It can be a valuable tool to obtain initial, useful

information about the electronic structure of three-dimensional solids in a short time, going to sizes far beyond the capability of reliable *ab initio* calculations.

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References

1. Dovesi, R.; Pisani, C.; Roetti, C.; Causa, M.; Saunders, V. R. CRYSTAL92: An Ab Initio Electron LCAO–Hartree–Fock Program for Periodic Systems. QCPE Program 577, 1992.
2. Blaha, P.; Schwarz, K.; Luitz, J. WIEN97: A Full-Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties, 1997.
3. Schedel-Niedrig, T.; Böhm, M. C.; Werner, H.; Schulte, J.; Schlögl, R. Phys Rev B, 1997, 55, 13542.
4. Böhm, M. C.; Schulte, J. Molec Phys 1996, 87, 735.
5. Ramírez, R.; Böhm, M. Int J Quantum Chem 1988, 34, 47.
6. Noga, J.; Baňacký, P.; Biskupič, S.; Pelikán, P.; Zajac, A. SOLID98, A Program System for Calculating Electronic Structure of Periodic Solid State Systems, S-Tech Inc, 1998.
7. Boča, R. Int J Quantum Chem 1987, 31, 941.
8. Boča, R. Int J Quantum Chem 1988, 34, 385.
9. Deák, P. Acta Phys Acad Sci Hung 1981, 50, 247.
10. Chandrasekhar, J.; Das, P. K. J Phys Chem 1992, 96, 679.
11. Bennet, A. J.; McCarrol, B.; Messmer, R. P. Surf Sci 1971, 24, 191.
12. Bennet, A. J.; McCarrol, B.; Messmer, R. P. Phys Rev B 1971, 3, 1397.
13. Zunger, A. J Phys C 1974, 7, 96; Zunger, A. J Chem Phys 1975, 62, 1861.; J Chem Phys 1975, 63, 1713.
14. André, J. M.; Gouverneur, L.; Leroy, G. Int J Quantum Chem 1967, 1, 427; J Chem Phys 1967, 1, 451.
15. Del Re, G.; Ladik, J. Biczó, G. Phys Rev 1967, 155, 997.
16. Varga, S.; Noga, J. To be published.
17. Suhai, S. J Chem Phys 1980, 73, 3843; Suhai, S.; Bagus, P. S.; Ladik, J. Chem Phys Lett 1982, 68, 497.
18. Ramirez, R.; Böhm, M. C. Phys Stat Sol B 1986, 135, 661.
19. Pisani, C.; Dovesi, R.; Roetti, C. Hartree–Fock Ab Initio Treatment of Crystalline Systems (Lecture Notes in Chemistry 48); Springer: Berlin, 1988.
20. Chadi, D. J.; Cohen, M. L. Phys Rev B 1973, 8, 5747.
21. Monkhorst, H. J.; Pack, D. J. Phys Rev B 1976, 13, 5188.
22. Evarestov, R. A.; Smirnov, V. P. Phys Stat Sol B 1983, 119, 9.
23. Ramirez, R.; Böhm, M. C. Int J Quantum Chem 1986, 30, 391.
24. Karpfen, A. Int J Quantum Chem 1981, 19, 1207.
25. Piela, L.; Delhalle, J. Int J Quantum Chem 1978, 13, 605; Delhalle, J.; Piela, L.; Bredas, J. L.; Andre, J. M. Phys Rev B 1980, 22, 6254.
26. Pople, J. A.; Beveridge, D. L. Approximate Molecular Orbital Theory; McGraw-Hill: New York, 1970, and references therein.
27. Goeppert-Mayer, M.; Sklar, A. L. J Chem Phys 1938, 6, 645.
28. Boča, R.; Pelikán, P. Coord Chem Rev 1992, 118, 1.
29. Madelung, O. (Ed.) Landolt–Börnstein New Series (Vol 17); Berlin: Springer; 1982.
30. Dovesi, R.; Pisani, C.; Ricca, F.; Roetti, C. Phys Rev B 1980, 22, 5936.
31. Dovesi, R.; Causà, M.; Angonoa, G. Phys Rev B 1981, 24, 4177.
32. Dovesi, R.; Pisani, C.; Roetti, C.; Dellarole, P. Phys Rev B 1981, 24, 4170.